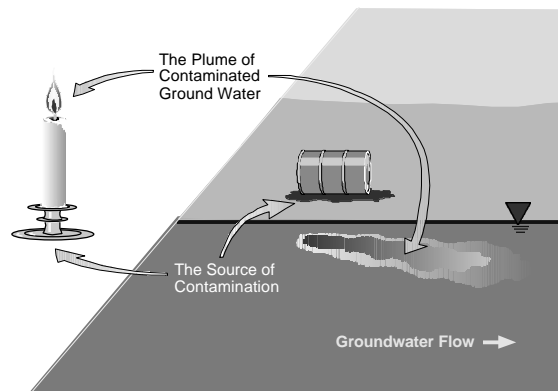

Estimating Biodegradation and Attenuation Rate Constants

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for printing purposes.**

Estimating Biodegradation and Attenuation Rate Constants

John T. Wilson

Office of Research and Development
National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio



Why Calculate Rate Constants?

- 1) Calculate concentrations at the point of attainment of standards
- 2) Compare rates at the site to literature to determine if the site is behaving like other sites
- 3) Predict changes caused by changes in flow velocity

Why Calculate Rate Constants?

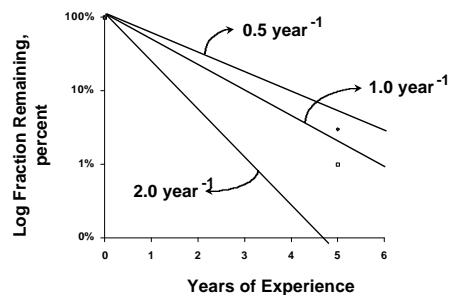
- 4) To determine how rapidly the ground water plume will clean up after the source is controlled.

Attenuation

First order rate constants?

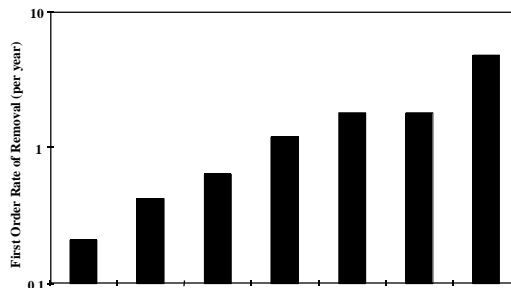
A first order rate of 1.0 per year equivalent to 2% a week or a half life of 8.3 months

First Order Rate Constants

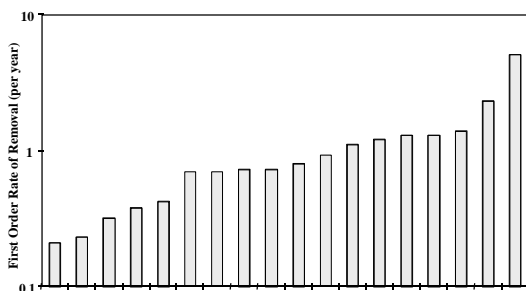


Literature Values for Natural Attenuation in Ground Water

TCE Attenuation in Microcosms



TCE Attenuation in Field



Literature Values for Natural Attenuation in Ground Water

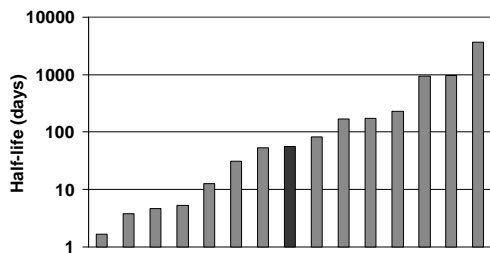
Anaerobic Biodegradation of Organic Chemicals in
Groundwater: A Summary of Field and Laboratory
Studies (SRC TR-97-0223F)

Dallas Aronson

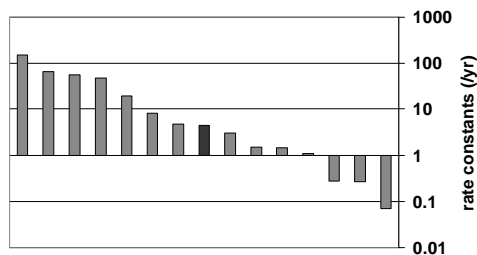
Philip Howard

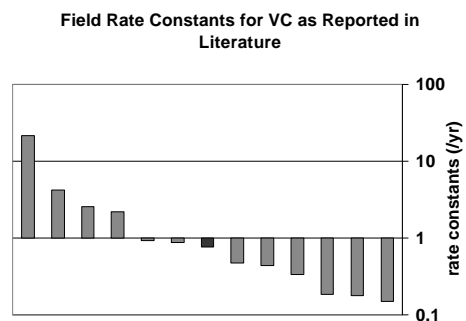
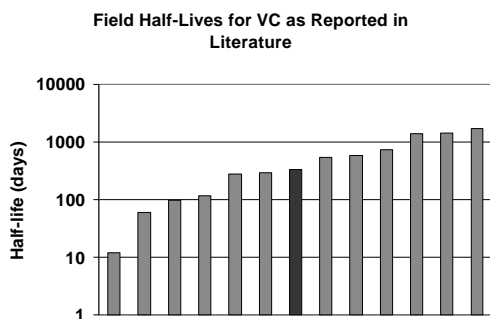
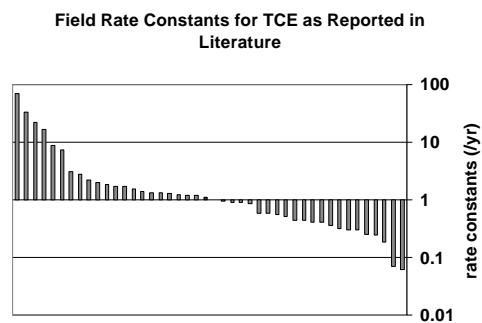
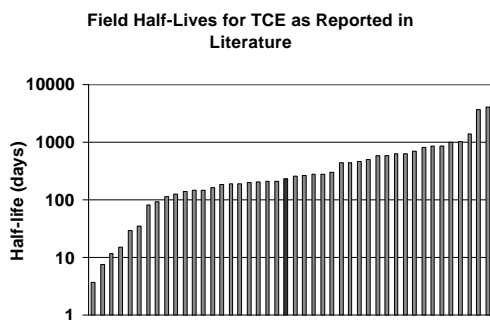
Environmental Science Center, Syracuse Research
Corporation, 6225 Running Ridge Road, North Syracuse,
NY 13212-2509

Field Half-Lives for PCE as Reported in Literature



Field Rate Constants for PCE as Reported in Literature





Field Data

Analyte	Number	Rate (per year)
PCE	4	4.0
TCE	18	1.1
cis-DCE	13	1.6
Vinyl chloride	6	1.3

Microcosm Studies

Analyte	Number	Rate (per year)
TCE	7	1.6
cis-DCE	3	4.3
Vinyl chloride	Fe III O ₂	4.0 4.2
1,1,1-TCA	3	2.0

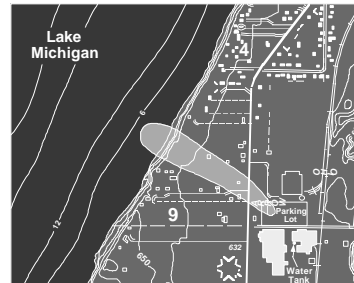
St. Joseph, Michigan

Case Study

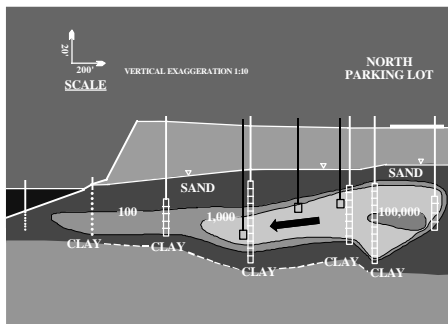
Natural Attenuation of TCE

Extracting Rate Constants

St. Joseph Site



St. Joseph Site



Vertical Transects (TRANSECTOR)

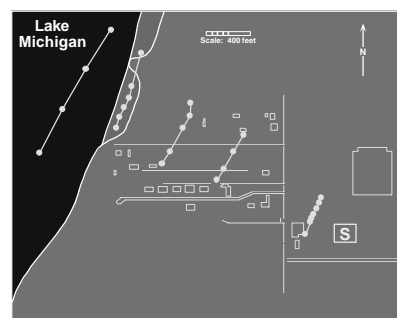
- Transects form logical units for studying sites
- Data in this form can be displayed in two-dimensions:

By representing the data as rectangles around each measurement point

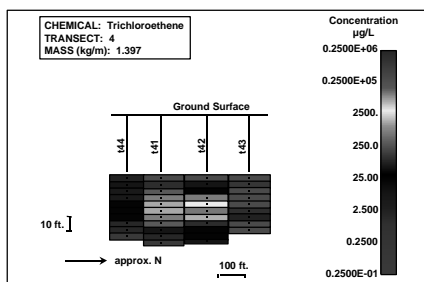
(chemical mass per unit thickness = porosity x concentration x length x width)

The transects provide much more spatial resolution than is usually available. They will be taken as ground truth to evaluate other approaches.

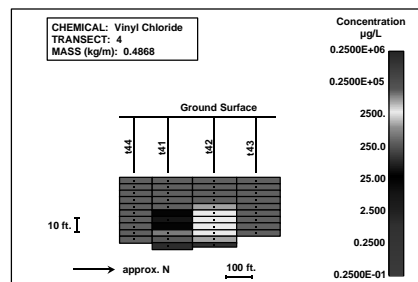
St. Joseph Site



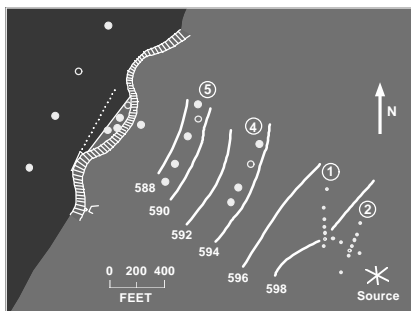
St. Joseph Site



St. Joseph Site



St. Joseph Site



Transect-Averaged Concentrations (µg/L) Dissolved Oxygen below 2.0 mg/L

Chemical	Transect 2	Transect 4	Transect 5	Lake Transect
TCE	7411	864	30.1	1.4
c-DCE	9117	1453	281	(0.80)
t-DCE	716	34.4	5.39	1.1
1,1-DCE	339	24.3	2.99	nd

Transect-Averaged Concentrations (µg/L) Dissolved Oxygen below 2.0 mg/L

Chemical	Transect 2	Transect 4	Transect 5	Lake Transect
TCE	7411	864	30.1	1.4
c-DCE	9117	1453	281	(0.80)
Vinyl Chloride	998	473	97.7	(0.16)

Transect-Averaged Concentrations (µg/L) Dissolved Oxygen below 2.0 mg/L

Chemical	Transect 2	Transect 4	Transect 5	Lake Transect
Ethene	480	297	24.2	no data
Sum of the Ethenes	19100	3150	442	3.5
Chloride	65073	78505	92023	44418

Apparent Loss Coefficients

$$\ln \left(\frac{c_{j+1}}{c_j} \right) = \lambda \cdot t$$

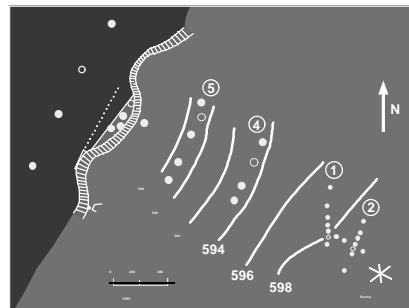
c_{j+1} = average concentration at the down gradient transect

c_j = average concentration at the up gradient transect

λ = apparent loss coefficient from transect j to j+1

t = travel time, determined from the seepage velocity, retardation factor and the distance

St. Joseph Site



For TCE from transect 2 to 4

$$t = 340 \text{ weeks}$$

$$c_{j+1} = 5.04 \times 10^{-4} \text{ kg/m}^3$$

$$c_j = 6.70 \times 10^{-3} \text{ kg/m}^3$$

$$\lambda = -0.38 / \text{year}$$

For TCE from transect 4 to 5

$$t = 145 \text{ weeks}$$

$$c_{j+1} = 1.44 \times 10^{-5} \text{ kg/m}^3$$

$$c_j = 5.04 \times 10^{-4} \text{ kg/m}^3$$

$$\lambda = -1.3 / \text{year}$$

Transect Pair	TCE	c-DCE	Vinyl Chloride
	Apparent change (per year)		
2 to 4	- 0.38	- 0.50	- 0.18
4 to 5	- 1.3	- 0.83	- 0.88
5 to Lake	- 0.94	- 3.1	- 2.2

Calculate Rate Constants

The next slides are a comparison of reconstructed hypothetical wells using data from the Keck Slotted Hollow Stem Auger technique to concentrations in real monitoring wells with short screens.

The whole approach requires properly constructed, properly installed, and properly maintained monitoring wells.

Transect 2

Compound	Reconstructed from slotted auger samples	RI Permanent Monitoring Well
	T-2-5	OW-19
	(mg/L)	
TCE	12.1	1.64
cis-DCE	33.7	4.63
Vinyl Chloride	2.3	2.4
Chloride	89.7	84.6

Transect 1

Compound	Reconstructed from slotted auger samples	RI Permanent Monitoring Well
	T-1-4	OW-18
	(mg/L)	
TCE	3.4	0.201
cis-DCE	11.2	0.413
Vinyl Chloride	3.7	0.922
Chloride	78.6	84.6

Transect 4

Compound	Reconstructed from slotted auger samples	RI Permanent Monitoring Well	RI Permanent Monitoring Well
	T-4-2	OW-29	OW-31
	(mg/L)		
TCE	1.3	<0.001	<0.001
cis-DCE	2.3	0.312	0.255
Vinyl Chloride	0.51	0.423	0.120
Chloride	98.9	31.1	81.1

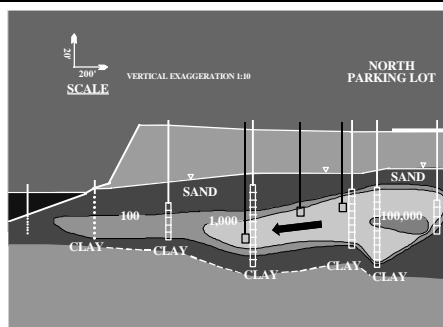
Transect 5

Compound	Reconstructed from slotted auger samples	RI Permanent Monitoring Well	RI Permanent Monitoring Well
	T-5-3	OW-32	OW-31
	(mg/L)		
TCE	0.035	0.0024	<0.001
cis-DCE	0.22	<0.001	0.255
Vinyl Chloride	0.063	<0.001	0.120
Chloride	63.6	16.2	81.1

Calculate Rate Constants

The next figure compares the screened intervals of the permanent monitoring wells to the intervals sampled by the Keck Slotted Auger technique.

St. Joseph Site



Calculate Rate Constants

The permanent wells may have been screened above or below the centerline "hot spot".

The permanent wells would have overestimated natural attenuation

We will use reconstructed concentrations from the Keck survey instead of the permanent monitoring wells.

Methods to Calculate Rate Constants

- 1) Method of Buscheck and Alcantar (1995)
- 2) Normalize to a conservative tracer
- 3) Calibrate a mathematical model

First-Order Decay Rate for a Steady State Plume

$$\lambda = \frac{v_c}{4\alpha_x} \left(\left[1 + 2\alpha_x \left(\frac{k}{v_x} \right) \right]^2 - 1 \right)$$

where:

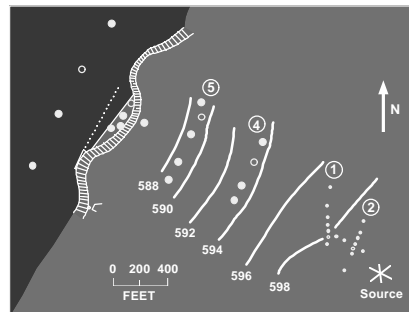
λ = first order biodegradation rate constant (approximate)

v_c = retarded contaminant velocity in the x-direction

α_x = dispersivity

k/v_x = slope of line formed by making a log-linear plot of contaminant concentration vs. distance downgradient along flow path

St. Joseph Site



Sampling Locations Along Centerline of Plume - St. Joseph

	T-2-5 0 ft	T-1-4 200 ft	T-4-2 1000 ft	T-5-3 1500 ft	55AE 2000 ft
	mg/L				
TCE	12.1	3.4	1.3	0.035	0.022
cis-DCE	33.7	11.2	2.3	0.22	0.42
Vinyl chloride	2.3	3.7	0.51	0.063	0.070
Organic chlorine	35.8	11.2	3.0	0.23	0.37

Method of Buscheck and Alcantar (1995)

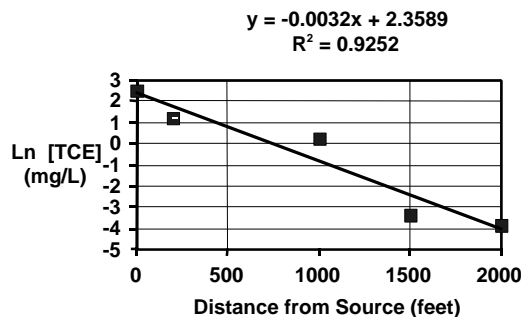
Linear Regression of Ln conc. TCE against distance along the flow path

Slope of the regression is k/v_x

Method of Buscheck and Alcantar (1995)

Distance (ft)	TCE (mg/L)	Ln conc. TCE
0	12.1	2.49
200	3.4	1.22
1000	1.3	0.262
1500	0.035	- 3.35
2000	0.022	- 3.82

St. Joseph Site



Method of Buscheck and Alcantar (1995)

$$R = 1 + K_{oc} f_{oc} \rho / \theta$$

$$K_{oc} = 120 \text{ mL/g}$$

$$f_{oc} = 0.001$$

$$\text{Porosity} = 0.3$$

$$\text{Bulk Density} = 1.7 \text{ g/cm}^3$$

$$\text{Retardation} = 1.7$$

Method of Buscheck and Alcantar (1995)

Contaminant velocity (V_c) equals seepage velocity divided by the retardation factor

$$V_c = 1.3 \text{ ft per day} / 1.7$$

$$= 0.76 \text{ ft per day}$$

$$= 277 \text{ ft per year}$$

Method of Buscheck and Alcantar (1995)

When

$$V_c = 277 \text{ ft per year}$$

$$\alpha_x = 100 \text{ feet}$$

$$k / V_x = -0.0032$$

Then

$$\lambda = -0.00165 \text{ per day}$$

$$= -0.602 \text{ per year}$$

Normalize to a Conservative Tracer

Will use the sum of chloride ion and organic chlorine as a tracer

Normalize to a Conservative Tracer

Multiply the concentration of chlorinated organic analytes by their mass fraction of chlorine

Sum the concentrations of chloride ion and organic chlorine in each chlorinated analyte

Mass Fraction Chlorine

Compound	Daltons	Daltons Chlorine	Mass Fraction Chlorine
PCE	166	142	0.855
TCE	137.5	106.5	0.810
DCE	97	71	0.732
Vinyl chloride	62.5	35.5	0.568

Sampling Locations Along Centerline of Plume - St. Joseph

	T-2-5 0 ft	T-1-4 200 ft	T-4-2 1000 ft	T-5-3 1500 ft	55AE 2000 ft
	----- mg/L -----				
Chloride	89.7	78.6	98.9	63.6	54.7
Organic Chlorine	35.8	11.2	3.0	0.23	0.37
Total Chlorine & Chloride	125.5	89.8	101.9	63.8	55.1

Normalize to a Conservative Tracer

Multiply the concentration of analyte down gradient by the dilution of the tracer to estimate the concentration expected in the absence of dilution

Calculation of Corrected Concentration

Where flow of ground water is from point A to point B:

$$C_{B, \text{Corr}} = C_B \left(\frac{\text{Chloride A}}{\text{Chloride B}} \right)$$

$C_{B, \text{Corr}}$ = corrected concentration of contaminant at point B

C_B = measured concentration of contaminant at point B

Chloride A = measured concentration of tracer at point A

Chloride B = measured concentration of tracer at point B

Normalize to a Conservative Tracer

From T-2-5 to 55AE, for TCE

$$\begin{aligned} \text{Corrected Concentration} &= \frac{0.022 \text{ mg/L (125.5 mg/L)}}{(55.1 \text{ mg/L})} \\ &= 0.050 \text{ mg/L} \end{aligned}$$

First-Order Decay

$$C = C_0 e^{-kt}$$

where:

C = contaminant concentration at time t

C₀ = initial contaminant concentration

k = first-order rate constant

Normalize to a Conservative Tracer

From T-2-5 to 55AE, for TCE

$$\frac{C_{(55AE)}}{C_{(T-2-5)}} = e^{-kt}$$

$$(0.050/12.1) = e^{-kt}$$

Normalize to a Conservative Tracer

$$\ln(0.050 / 12.1) = -kt$$

$$-5.49 = -kt$$

$$k = 5.49 / t$$

Normalize to a Conservative Tracer

The locations are 2,000 feet apart.

If the seepage velocity is 1.3 feet per day,

the retarded TCE velocity = 1.3 / 1.7 feet per day
= 0.76 feet per day

Normalize to a Conservative Tracer

The travel time = 2,000 feet / 0.76 feet per day
= 2,631 days

Normalize to a Conservative Tracer

$$k = 5.49 / 2,631 \text{ days} \\ = -0.00208 / \text{day} \\ = -0.76 / \text{year}$$

Comparison of Rate Constants

Normalize to a conservative tracer
= -0.76 per year

Method of Buscheck and Alcantar
= -0.602 per year

Transect comparisons

= -0.94 per year
= -1.3 per year
= -0.38 per year

Calibrate BIOSCREEN

West Plume at St. Joseph, Michigan

BIOSCREEN Natural Attenuation Decision Support System
Version 1.4

1. HYDROGEOLOGY
Storage Velocity* V_s 492.8 (ft/yr)
Hydraulic Conductivity K 0.02 (cm/sec)
Hydraulic Gradient I 0.007 (ft/ft)
Porosity n 0.3 ()

2. DISPERSION
Longitudinal Dispersion* α_L 32.3 (ft)
Transverse Dispersion* α_T 3.2 (ft)
Vertical Dispersion* α_V 3.0 (ft)
Estimated Plume Length L_p 2000 (ft)

3. ADSORPTION
Retardation Factor* R 1.7 ()
Soil Bulk Density ρ_b 1.7 (g/cc)
Partition Coefficient K_{oc} 120 (L/kg)
Fraction Organic Carbon f_{oc} 1.0E-3 ()

4. BIODEGRADATION
1st Order Decay Coef* λ 0.1 (per yr)
Solubility Half-Life $t_{1/2}$ 115 (days)
or Instantaneous Reaction Model
Delta Oxygen* ΔO_2 0 (mg/L)
Delta Nitrate* ΔNO_3 0 (mg/L)
Observed Ferrous Iron* Fe^{2+} 0 (mg/L)
Delta Sulfate* ΔSO_4 0 (mg/L)
Observed Methane* CH_4 0 (mg/L)

5. GENERAL
Model Area Length* 2000 (ft)
Model Area Width* 500 (ft)
Simulation Time* 10 (yr)

6. SOURCE DATA
Source Thickness in Sat. Zone* 80 (ft)
Source Zones:
Zone 1: 120 1
Zone 2: 40 7
Zone 3: 60 14
Zone 4: 60 7
Zone 5: 120 1
Source Release Rate (mg/yr) 10000
Initial Source Concentration (mg/L) 10000
In Source NAPL Solubility (mg/L) 10000
Dist. from Source (ft) 0 200 400 600 800 1000 1200 1400 1600 1800 2000

7. FIELD DATA FOR COMPARISON
Concentration (mg/L) 12.1 1.4 1.3 0.05 0.02
Dist. from Source (ft) 0 200 400 600 800 1000 1200 1400 1600 1800 2000

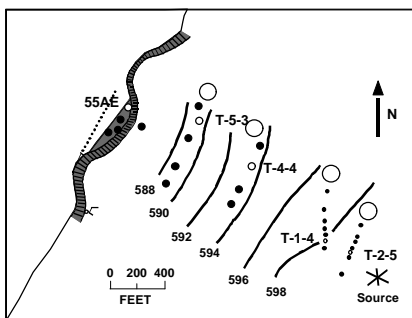
8. CHOOSE TYPE OF OUTPUT TO SEE:
RUN CENTERLINE
RUN ARRAY
View Output
View Output
Help
Recalculate This Sheet
Paste Example Dataset
Restore Formulas for V_s , Dispersivities, R , lambda, other

See following page for a full-size version of the slide.

Calibrate BIOSCREEN

Use the next figure to estimate the hydraulic gradient

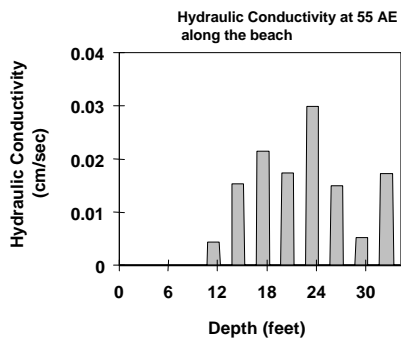
St. Joseph Site



The average hydraulic conductivity is 50 feet per day or 0.02 cm per sec.

**Table is missing but will be added in the
near future.**

Thank you for your patience.



1. HYDROGEOLOGY			
Seepage Velocity*	Vs		482.8
or			
Hydraulic Conductivity	K		2.0E-02
Hydraulic Gradient	i		0.007
Porosity	n		0.3
2. DISPERSION			
Longitudinal Dispersivity*	alpha x		32.3
Transverse Dispersivity*	alpha y		3.2
Vertical Dispersivity*	alpha z		0.0
or			
Estimated Plume Length	Lp		2000

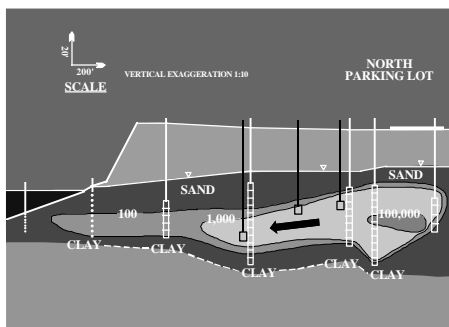
4. BIODEGRADATION			
1st Order Decay Coeff*	lambda		6.0E-1 (per yr)
or			
Solute Half-Life	t-half		1.15 (year)
or Instantaneous Reaction Model			
Delta Oxygen*	DO		0 (mg/L)
Delta Nitrate*	NO3		0 (mg/L)
Observed Ferrous Iron*	Fe2+		0 (mg/L)
Delta Sulfate*	SO4		0 (mg/L)
Observed Methane*	CH4		0 (mg/L)

Calibrate BIOSCREEN

Use the next figure to estimate the geometry of the plume.

The vertical scale bar in the upper left corner represents 20 feet.

St. Joseph Site



5. GENERAL

Modeled Area Length*

2000 (ft)

Modeled Area Width*

500 (ft)

Simulation Time*

10 (yr)

6. SOURCE DATA

Source Thickness in Sat. Zone*

80 (ft)

Source Zones:

Width* (ft)

Conc. (mg/L)*

L

W

Vertical Section for Zone

Calibrate BIOSCREEN

Use the next figure to set up the lanes in BIOSCREEN for TCE attenuation.

Sampling locations along upstream transect

T2-7 T2-2 T2-5 T2-1 T2-6 T2-4 T2-2

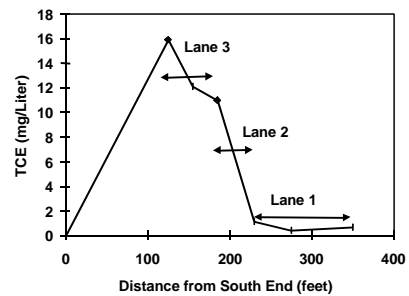
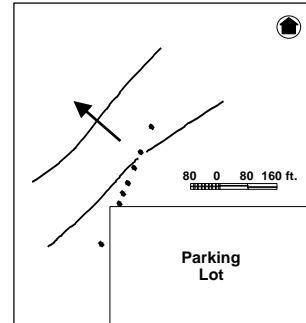
Distance from south end of transect, feet

0 125 155 185 230 275 350

Average conc. TCE, mg/liter

0.02 15.9 12.1 11.0 1.1 0.39 0.68

St. Joseph Site



6. SOURCE DATA

Source Thickness in Sat. Zone* (ft)

Source Zones:

Width* (ft)	Conc. (mg/L)*
120	1
45	7
60	14
45	7
120	1

Source Half-life (see Help):

>1000 (yr)

Inst. React. 1st Order

Soluble Mass (Kg)

In Source NAPL Soil

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3

View of Plume Looking Down

Observed Centerline Concentrations at Monitoring Wells
If No Data Leave Blank or Enter "0"

7. FIELD DATA FOR COMPARISON

Concentration (mg/L)	12.1	3.4		1.3		.035	.022	
Dist. from Source (ft)	0	200	600	800	1200	1400	1800	2000

Calibrate BIOSCREEN

Use the next table to set up field data in BIOSCREEN for attenuation of TCE.

Sampling Locations Along Centerline of Plume - St. Joseph

	T-2-5 0 ft	T-1-4 200 ft	T-4-2 1000 ft	T-5-3 1500 ft	55AE 2000 ft
	mg/L				
TCE	12.1	3.4	1.3	0.035	0.022
cis-DCE	33.7	11.2	2.3	0.22	0.42
Vinyl chloride	2.3	3.7	0.51	0.063	0.070

7. FIELD DATA FOR COMPARISON

Concentration (mg/L)	12.1	3.4			1.3			.035	.022		
Dist. from Source (ft)	0	200	400	600	800	1000	1200	1400	1600	1800	2000

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN CENTERLINE

View Output

RUN ARRAY

View Output

Help

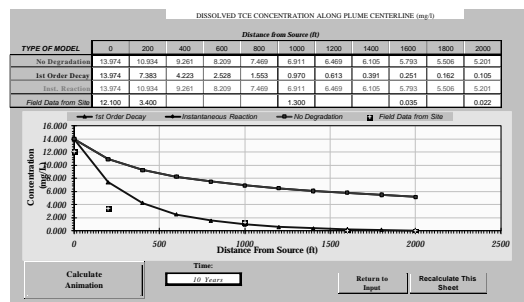
Recalculate This Sheet

Paste Example Dataset

Restore Formulas for Vs, Dispersivities, R, lambda, other

Calibrate BIOSCREEN

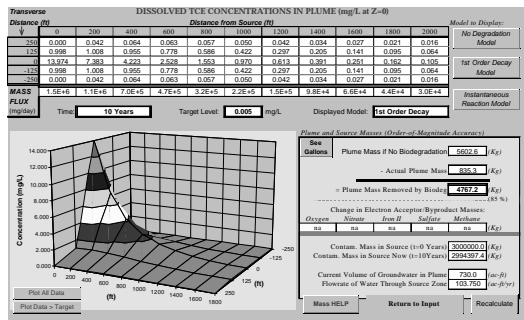
Results from RUN CENTERLINE



See following page(s) for a full-size version of the slide.

Calibrate BIOSCREEN

Results from RUN ARRAY



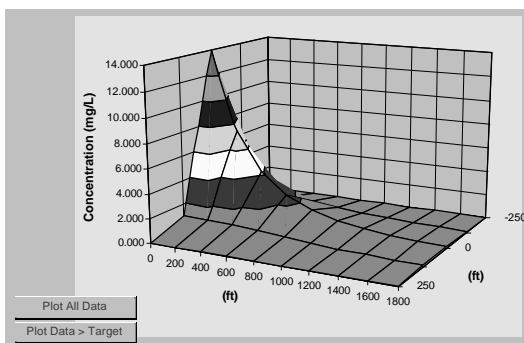
See following page(s) for a full-size version of the slide.

**Table is missing but will be added in the
near future.**

Thank you for your patience.

**Table is missing but will be added in the
near future.**

Thank you for your patience.



Plume and Source Masses (Order-of-Magnitude Accuracy)

See Gallons

Plume Mass if No Biodegradation: 5602.6 (Kg)

- Actual Plume Mass: 835.3 (Kg)

= Plume Mass Removed by Biodeg: **4767.2** (Kg) (85 %)

Change in Electron Acceptor/Byproduct Masses:

Oxygen	Nitrate	Iron II	Sulfate	Methane
na	na	na	na	na

(Kg)

Contam. Mass in Source (t=0 Years): 3000000.0 (Kg)

Contam. Mass in Source Now (t=10 Years): 2994397.4 (Kg)

Current Volume of Groundwater in Plume: 730.0 (ac-ft)

Flowrate of Water Through Source Zone: 103.750 (ac-ft/yr)

Mass HELP **Return to Input** Recalculate

Calibrate BIOSCREEN

1.0 acre foot per year =

3.4 cubic meters per day

0.62 gallons per minute

100 acre feet per year =

0.09 million gallons per day

Sources of information

BIOSCREEN

BIOSCREEN and BIOPLUME III are available on the NRMRL/SPRD Web page:

<http://www.epa.gov/ada/kerrlab.html>

Information by Phone, FAX, or Mail

- NCEPI
 - Order documents and databases with "EPA" document numbers free of charge
 - FAX requests to 513-489-8695
 - Mail requests to NCEPI, PO Box 42419, Cincinnati, OH 45242
- NTIS
 - Purchase products with "PB" document numbers
 - Order by phone at 703-487-4650 or 800-553-NTIS (for rush service)

TIO Information Online

- **Clean-up Information (CLU-IN) System**
 - **WWW site**
 - <http://clu-in.com>
 - Go to “Publications and Software” area to download publications and databases